

Physical properties of saturated estolides and their 2-ethylhexyl esters[☆]

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Abstract

Biodegradable, vegetable oil-based lubricants must have better low temperature properties before they can become widely acceptable in the marketplace. These low temperature properties are usually measured as the material's pour point, the minimum temperature at which a material will still pour. Viscosity and viscosity index also provide information about a fluid's properties where a high viscosity index denotes that a fluid has little viscosity change over a wide temperature range. Oleic acid and a series of saturated fatty acids, butyric through stearic, were treated with 0.4 equivalents of perchloric acid at either 45 or 55 °C to produce complex estolides, dimers and tetramers of fatty acids linked through the double bond and carbonyl group. Yields varied between 45 and 65% after Kugelrohr distillation. The estolide number (EN), the average number of fatty acid units added to a base fatty acid, varied with reaction temperature as well as with the change in saturated fatty acids. The saturate-capped, oleic estolides were esterified with 2-ethylhexanol to obtain high yields of the corresponding ester. As the chain length of saturate capping material increased from C-4 to C-10, the low temperature performance of the estolide 2-ethylhexyl esters, namely pour point, decreased to –39 °C. The other mid-chain, saturated estolide 2-ethylhexyl esters C-6 through C-14 also had superior low temperature properties compared with their competitors; i.e. soy-based, synthetic-based and petroleum-based oils. The amount of oligomerization (EN) had an important role with the viscosities. Viscosity increased with higher oligomerization and the free acid estolides were generally several hundred centistokes (cSt) more viscous than the corresponding esters. The viscosity index ranged from 122 to 155 for the free acids estolides while the estolide 2-ethylhexyl esters had slightly higher indices which ranged from 172 to 196. These new estolide esters displayed far superior low temperature properties, and were more suitable as a base stock for biodegradable lubricants and functional fluids than current commercial materials. © 2002 Published by Elsevier Science B.V.

Keywords: Estolides; Oleic; Pour point; Cloud point; Viscosity; Saturated fatty acids; Low temperature storage

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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1. Introduction

Vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties for which they are being more closely examined as a base stock for lubricants and functional fluids (Zaher and Nomany, 1988; Mang, 1994, 1997; Legrand and Durr, 1998; Canter, 2001). Two major problems with vegetable oils as functional fluids are low resistance to thermal oxidative stability (Becker and Knorr, 1996) and poor low temperature properties (Asadauskas and Erhan, 1999; Zehler, 2001). However, with the addition of additives these properties can sometimes be improved, but only at the sacrifice of biodegradability, toxicity, and cost.

Vegetable oils and their derivatives show superior biodegradability compared with petroleum oils (Novick et al., 1996) and synthetic esters in actual field studies (Haigh, 1994, 1995). Vegetable oils and synthetic esters also have superior viscosity indices (Noureddini et al., 1992) and lubricating properties compared with mineral oils. The coefficient of friction for vegetable oils is nearly one-half that of refined mineral oils (Mang, 1997).

Estolides and estolide esters from meadowfoam (Isbell and Kleiman, 1996), oleic (Isbell et al., 2001), castor oil, or any sources of hydroxy fatty acids (Zoleski and Gaetani, 1984) show promise

as cosmetics, coatings, and biodegradable lubricants. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters. The estolide number (EN) is defined as the average number of fatty acids added to the base fatty acid (Fig. 1, $EN = n + 1$).

Estolides from oleic acid when synthesized under various acidic conditions with mineral acids provides the best yields and physical properties. When one equivalent of HClO_4 at 50 °C is used, estolide yields average about 76% (Isbell and Kleiman, 1996). The reaction produces a light-colored material that could be used without further distillation. The use of H_2SO_4 as a catalyst tends to lead to sulfonated by-products that decompose over time. Sulfonic acid moieties are released to decrease the pH of the estolide solution and impair the function of the fluid. In contrast, HClO_4 reaction which provides a pH-stable estolide.

A series of saturated estolides were developed by Cermak and Isbell (2001) in which oleic acid and saturated fatty acids ranging from, butyric through stearic, treated with 0.4 equivalents of perchloric acid at either 45 or 55 °C produce complex estolides (Fig. 1). Yields varied between 45 and 65% after Kugelrohr distillation. The EN varied with reaction temperature as well as with the change in saturated fatty acids. The shorter-

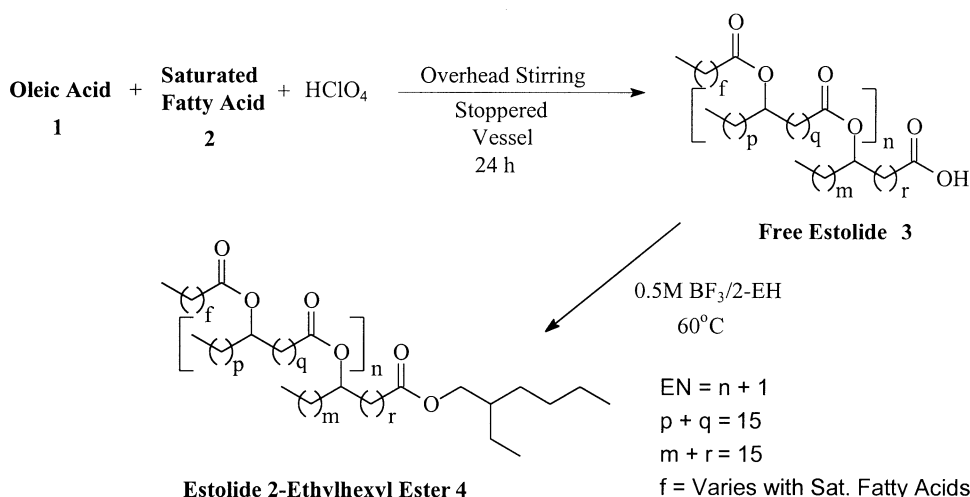


Fig. 1. Reaction scheme for the formation of the estolides and its 2-ethylhexyl ester.

chain, saturated fatty acids, i.e. butyric and hexanoic acid, provide material with higher degrees of oligomerization ($EN = 3.3$) than stearic acid ($EN = 1.4$). These new saturated estolides and estolide esters show very different physical properties and types of by-products.

These new estolides have certain properties that could help eliminate common problems associated with vegetable oils as functional fluids. One of the concerns with vegetable oils is their stability toward oxidation. Simple oleic estolides when formulated with a small amount of oxidative stability package show better oxidative stability than both petroleum and vegetable oil-based fluids (unpublished data), but there is still room for improvement. There are a number of ways to improve the oxidative stability of an oil. Akoh (1994) reported that refined soybean oil has an oxidative stability index, OSI, of 9.4 h at 110 °C, but once the oil is partially hydrogenated the OSI is increased to 15.3 h at 110 °C, an improvement of more than 60%. The same approach was taken with the oleic estolides, where hydrogenation with 2% w/w of 10% palladium on activated carbon as catalyst gave completely saturated estolides (Isbell et al., 2001). The saturated oleic estolides are expected to be more oxidatively stable than the unsaturated estolides, assuming the same trend displayed by soybean oil holds true.

However, in the cases examined by Isbell et al. (2001), in which a new saturated estolide was synthesized via hydrogenation, the new saturated estolide had a high pour point of -9 °C, which is unsatisfactory for a functional fluid. Cermak and Isbell (2001) envisioned a new class of saturated estolides with superior low temperature properties. Thus, by varying the capping material on the estolide, the crystal lattice structure of the material could be disrupted as it approached its pour point. This would lead to superior pour points, cloud points and other low temperature properties.

Estolides and estolide esters compare favorably with commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids, and petroleum oils. In this paper, we report the physical properties, such as pour and cloud points, viscosity, and other low temperature

properties, of these new saturated fatty acid capped estolides and their corresponding esters. These new saturated estolides, which should have superior biodegradability and lubricating properties compared with petroleum products, were compared with commercially available materials based on their low temperature properties.

2. Materials and methods

2.1. Materials

Petroleum oil: Mobil® 10W-30 and synthetic oil: Castrol Synthetic® 10W-30 were obtained from Wal-Mart Department Store® (Peoria, IL). Soy-based oil: Biosoy® was obtained as a free sample from University of Northern Iowa (Cedar Falls, IA). Hydraulic fluid: Traveler Universal Hydraulic Fluid® was obtained from Tractor Supply Company® (Peoria, IL)

2.2. Gardner color

Gardner color was measured on a Lovibond 3-Field Comparator from Tintometer Ltd. (Salisbury, England) using AOCS method Td 1a-64 (Firestone, 1994). Gardner color of both the residue and distillate materials was measured throughout the distillation. The + and – notation was employed to designate samples that did not match one particular color or, in the case of the residue, an 18+ represented a color darker than the upper limit of 18.

2.3. Viscosity

Viscosity was measured using a calibrated Cannon–Fenske viscometer tube purchased from Cannon Instrument Co. (State College, PA) in a Temp-Trol (Precision Scientific, Chicago, IL) viscometer bath set at 40.0 and 100.0 °C. Viscosity and viscosity index were calculated using ASTM methods D 445-65 (American Society for Testing Materials, 1991) and ASTM D2270-79 (American Society for Testing Materials, 1991), respectively. All viscosity measurements were run in duplicate and the average values are reported.

2.4. Pour point

Pour points were measured by ASTM method D97-96a (American Society for Testing Materials, 1996) to an accuracy of ± 3 °C. The pour points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged into a cooling media. The sample temperature was measured in 3 °C increments at the top of the sample until it stopped pouring. This point was reached when the material in the test jar did not flow when held in a horizontal position for 5 s. The temperature of the cooling media was determined based on the expected pour point of the material. Samples with pour points that ranged from (+9 to -6, -6 to -24, and -24 to -42 °C) were placed in baths of temperature (-18, -33, and -51 °C), respectively. The pour point was defined as the coldest temperature at which the sample still poured. All pour points were run in duplicate and the average values were reported.

2.5. Cloud point

Cloud points were determined by ASTM method D2500-99 (American Society for Testing Materials, 1999) to an accuracy of ± 1 °C. The cloud points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged into a cooling media. The sample temperature was measured in 1 °C increments at the bottom of the sample until cloudiness was observed at the bottom of the test jar. The temperature of the cooling media was determined based on the expected cloud point of the material. Samples with cloud points that ranged from (room temperature to 10, 9 to -6, and -6 to -24, -24 to -42 °C) were placed in baths of temperature (0, -18, -33, and -51 °C), respectively. Cloud points were run in duplicate and the average values were reported.

2.6. Low temperature storage

Low temperature storage points were determined by Caterpillar Inc. BF-1 Specification for Hi- Performance Biodegradable Hydraulic Fluid (Caterpillar, 1997) of ± 1 day. The low tempera-

ture points were determined with the same test jars and sample amount as ASTM D 97-96a. The samples were first heated to 50 °C for 30 min, cooled to room temperature and then stoppered. The samples were tested at three different specified temperatures (e.g. 0, -15, and -25 °C) and visually inspected every 24 h for 7 days. Failing criteria consisted of crystallization, solidification, and formation of solid particulate, but did not include haziness or loss of transparency.

2.7. Estolides and estolide 2-ethylhexyl esters

Estolides and estolide 2-ethylhexyl esters were synthesized as previously reported (Cermak and Isbell, 2001).

3. Results and discussion

A series of estolides and estolide 2-ethylhexyl esters were synthesized from oleic acid and the appropriate saturated fatty acid with 0.4 mole equivalents of perchloric acid at either 45 or 55 °C for 24 h, Fig. 1. Vacuum distillation removed any excess fatty acids and provided estolide samples. The alcohol portion of the ester functionality was determined by Isbell et al. (2001) to have a significant role in pour point reductions, because branched chain alcohols dramatically lower the pour point. Thus, these estolides were converted to their corresponding 2-ethylhexyl estolide esters by the addition of 0.5 M 2-ethylhexanol/ BF_3 at 60 °C for 2–4 h for enhanced pour point capability. Samples were vacuum distilled to remove any excess 2-ethylhexanol, providing neat estolide 2-ethylhexyl ester samples. The reaction temperatures, saturated fatty acids, percent yields, color, and ENs are listed in Table 1. Pour and cloud points, viscosity, viscosity index, and low temperature storage data determined for each estolide and estolide 2-ethylhexyl ester samples are listed in Tables 2 and 3.

The pour points of saturated estolides and estolide 2-ethylhexyl esters synthesized at 45 °C are displayed in Fig. 2. As the chain length of the saturated fatty acid component increased from

Table 1

Acid catalyzed condensation reaction with oleic acid and varying saturated fatty acids

Estolide	Saturated fatty acid	Temperature (°C)	Estolides ^a (%)	Capped ^b (%)	Gardner color
OB-45	Butyric	45	53.9	33	8
OB-55	Butyric	55	47.4	39	11
OC-45	Caproic	45	57.0	34	9
OC-55	Caproic	55	51.7	31	11
OO-45	Octanoic	45	58.8	42	10
OO-55	Octanoic	55	48.9	34	12
OD-45	Decanoic	45	64.8	53	18
OD-55	Decanoic	55	56.4	57	18
OL-45	Lauric	45	63.7	58	7
OL-55	Lauric	55	60.1	60	11
OM-45	Myristic	45	64.0	65	6
OM-55	Myristic	55	54.6	65	10
OP-45	Palmitic	45	58.5	68	8
OP-55	Palmitic	55	58.6	63	10
OS-45	Stearic	45	48.7	43	11
OS-55	Stearic	55	44.5	65	11

Reactions were run for 24 h with overhead stirring in a 2:1 mol ratio, oleic:saturated fatty acids with 0.4 mol equivalents of perchloric acid.

^a Yield based on mass of pure estolide obtained via distillation.

^b Ratio of estolide capped with saturated fatty acids determined by GC (SP 2380, 30 m × 0.25 mm i.d.).

Table 2

Physical properties of acid catalyzed condensation reaction with oleic acid and varying saturated fatty acids

Estolide ^a	GC EN	Pour point (°C)	Cloud point (°C)	Viscosity @ 40 °C (cSt)	Viscosity @ 100 °C (cSt)	Viscosity index
OB-45	3.3	−27	−26	410.0	39.9	146
OB-55	2.6	−18	−10	456.0	41.7	155
OC-45	3.3	−24	−27	515.5	39.7	122
OC-55	3.1	−21	−17	411.2	40.3	148
OO-45	2.9	−24	−24	389.1	37.7	143
OO-55	2.6	−18	−9	398.1	39.2	147
OD-45	2.7	−21	− ^b	342.0	34.0	142
OD-55	2.5	−21	− ^b	336.9	34.3	145
OL-45	2.2	−25	−27	262.6	28.7	145
OL-55	2.1	−16	−18	262.4	28.4	143
OM-45	1.8	−18	−6	282.3	30.4	146
OM-55	1.8	−9	7	290.5	30.0	140
OP-45	1.9	−10	−12	267.1	28.7	143
OP-55	1.7	−2	−2	236.4	26.5	145
OS-45	1.4	−3	−2	296.5	31.0	143
OS-55	1.4	3	19	296.6	30.6	141

Reactions were run for 24 h with overhead stirring in a 2:1 mole ratio, oleic:saturated fatty acids with 0.4 mole equivalents of perchloric acid.

^a Yield based on mass of pure estolide obtained via distillation.

^b Material color to dark to determine accurate cloud point.

Table 3
Properties of 2-ethylhexyl estolides esters

Estolide ester ^a	GC EN	Pour point (°C)	Cloud point (°C)	Viscosity @ 40 °C (cSt)	Viscosity @100 °C (cSt)	Viscosity index	Passes 7-day test ^b (°C)
OB-EH-45	2.8	−30	−36	125.5	19.3	175	−15
OB-EH-55	3.0	−19	−17	131.3	20.0	175	−15
OC-EH-45	3.5	−30	−34	114.5	17.9	174	−25
OC-EH-55	2.7	−27	−30	106.0	16.9	173	−25
OO-EH-45	3.0	−36	−41	104.4	16.8	175	−25
OO-EH-55	3.1	−24	−16	106.3	16.8	172	−15
OD-EH-45	2.7	−39	— ^c	93.8	15.5	176	— ^c
OD-EH-55	2.3	−24	— ^c	84.2	14.3	177	— ^c
OL-EH-45	2.2	−36	−32	73.9	13.0	179	−25
OL-EH-55	1.9	−27	−29	70.6	12.4	176	−25
OM-EH-45	2.0	−25	−22	80.5	13.9	179	−25
OM-EH-55	1.8	−18	−11	78.7	13.4	174	0
OP-EH-45	1.4	−12	−13	81.6	13.5	174	−15
OP-EH-55	1.1	−12	−13	41.3	8.7	196	0
OS-EH-45	1.1	−15	−4	81.8	14.0	177	−15
OS-EH-55	1.1	−5	−1	77.1	13.4	178	0

^a 2-Ethylhexyl ester.

^b BF-1 specification for hi-performance bio-degradable hydraulic fluid.

^c Material color too dark to determine accurate values.

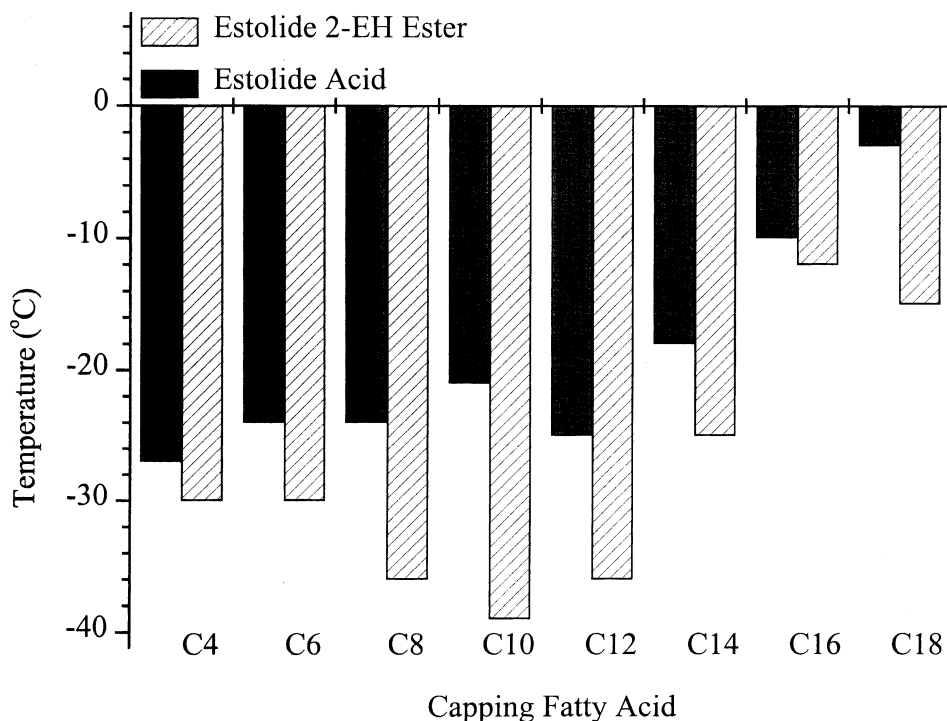


Fig. 2. Effect on pour point with saturated fatty acid at 45 °C.

Table 4

Comparison of low temperature properties and viscosity index of oleic-octanoate estolide 2-EH ester to that of commercial lubricants

Lubricant ^a	Pour point (°C)	Cloud point (°C)	Passes 7-day test ^b (°C)	Viscosity index
Commercial petroleum oil	−27	2	0	152
Commercial synthetic oil	−21	−10	−15	174
Commercial soy based oil	−18	1	− ^c	220
Commercial hydraulic fluid	−33	1	−15	146
OO-EH-45 ^d (Table 3)	−36	−41	−25	175

^a Commercial fully formulated material from local vendors.

^b Low temperature storage test.

^c Only lasted 5 days at 0 °C.

^d Unformulated.

C-4 to C-10, the pour points of the estolide 2-ethylhexyl esters decreased to −39 °C, then as the chain length increased to C-18 the pour points increased to −15 °C. The differences in pour point of the estolide versus the estolide 2-ethylhexyl esters. In very case, the estolide 2-ethylhexyl esters had better (lower) pour points than their corresponding free acid estolides. As the chain length increased, the pour points do not vary much for the estolide 2-ethylhexyl esters until C-16 and -18, when the pour point increased. The C-18 estolide 2-ethylhexyl ester synthesized under the proceeding conditions matched the pour point of material synthesized by Isbell et al. (2001) where the oleic estolie 2-ethylhexyl ester was hydrogenated to the saturated material. Isbell et al. (2001) reported that estolides that underwent hydrogenation showed a dramatic increase in the pour point, so that one would expect that the mid-chain saturated fatty acids would have higher pour points then those observed.

The cloud points of saturated estolides and estolide 2-ethylhexyl esters synthesized at 45 °C followed the same general trend as the pour points in Fig. 2 (Tables 2 and 3). In general, all distilled estolides with low pour points also have low cloud points. The C-10 estolide 2-ethylhexyl ester (OD-EH-45 Table 3) should have had the best cloud point, but the material was much too darkly colored to determine the cloud point. A Gardner color of 18 is a non-transparent black material.

The low temperature storage values are summarized in Table 4. Three different temperature ranges

were explored to show the possibility of crystallization, solidification, and formation of solid particulate for each estolide 2-ethylhexyl ester. In general, all the estolide esters passed the 7-day cold storage test (Caterpillar, 1997) at 0 °C, but only the top performing estolides passed this test at −25 °C. Again, as with the pour and cloud points, the C-6 through C-14 estolide esters made at 45 °C were the best performers. When stored at −15 °C, there was a true distinction between the products from the 45 and 55 °C reactions in terms of low temperature properties. The 45 °C reaction produced estolide esters with better low temperature storage properties than the 55 °C series.

The viscosities are relatively average for all of the estolide 2-ethylhexyl esters with an approximate range of 41–131 centistokes (cSt). The free acid estolides, as expected, had higher viscosities then the esters, with an approximate range of 236–515 cSt caused by hydrogen bonding of the carboxylate functionality.

Viscosities of the estolide 2-ethylhexyl esters increased in an exponential manner with the EN (degree of oligomerization), as shown in Fig. 3. This same general trend was observed by Isbell et al. (2001) with the simple oleic estolide 2-ethylhexyl esters. The viscosity range of the estolides and estolide 2-ethylhexyl esters has proven to be useful for numerous applications.

The physical properties of various commercial materials were compared with the better performing estolide 2-ethylhexyl ester (Table 4). The estolide 2-ethylhexyl ester chosen for comparison to

the commercial products was not the best performer in Table 3 (OD-EH-45), because the decanoate estolide was too dark. Thus, the second best material, a C-8 saturated estolide 2-ethylhexyl ester (OO-EH-45 Table 3), was used instead. The C-8 saturated estolide 2-ethylhexyl ester was completely unformulated, unlike the commercial products that contained up to 40% additives to improve cold temperature properties. All the commercial products in Table 4 have functional pour points except the soy-based oil. Soy-based products have been demonstrated earlier to have pour points too high for cold weather climates (Erhan and Asadauskas, 2000). All of the commercial products listed had high cloud points compared with the estolide 2-ethylhexyl ester. A high cloud point could lead to filter plugging and poor pumpability in cold weather applications, thus there is a need for a better cold weather performing oil. In the low temperature test, only the estolide passed the lower temperature range, whereas the soy-based material solidified after 5 days at 0 °C. Viscosity index denotes a fluid that will have little viscosity change over a wide temperature range. The estolide ester has one of the highest viscosity indices compared with commercial products.

4. Conclusions

Estolides from oleic and saturated fatty acids and their 2-ethylhexyl esters have excellent low temper-

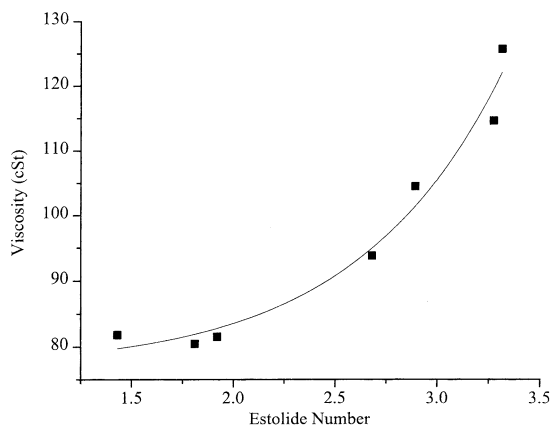


Fig. 3. Effect of saturated estolide oligomerization on viscosity.

ature properties. The estolides synthesized at 45 °C produce materials that have especially good low temperature properties. In the best case, oleic-decanoate estolide 2-ethylhexyl ester, OD-EH-45, was produced with a pour point of −39 °C. In general, all the saturated estolide esters have excellent cloud points and perform well in the low temperature storage test.

Viscosity is dictated by the amount of oligomerization, as the amount of oligomerization increased so did the viscosities and the free acid estolides were generally several hundred cSt more viscous than the corresponding ester. The estolides had very wide viscosity ranges as shown in Table 2. Thus there are many potential industrial applications for such materials.

These new saturated, fatty acid-capped estolides and corresponding esters have outperformed commercial products in cold temperature properties even though the estolides were unformulated.

5. Uncited references

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